

SPG (Shirasu Porous Glass) and its Application

Tadao NAKASHIMA

Ind. Res. Inst. of Miyazaki Prefecture
1-7-14 Tsunehisa, Miyazaki-shi 880

Porous glass has been attracting attention as a material that permits formation of a unique microstructure and design of pores and, as such, it is expected to find a wide range of application.

The authors have developed a new type of porous glass synthesized from $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ type glass which was made from "Shirasu", material available in large quantities in the southern part of Kyushu, Japan, and was named this new type of glass as SPG. This glass is unique in the chemical composition and its controllable pore size, and is drawing interest for its filtering and adsorbing capabilities.

1. Introduction

In recent years, porous glass has been attracting special attention as a material that permits formation of a unique microstructure and design¹⁾ of pores and it is expected to find application in various fields of industry^{2,3)}. The glass that was studied in the earlier stage was $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ type glass⁴⁾, which was made by utilizing phase separation of $\text{Na}_2\text{O-B}_2\text{O}_3$ and SiO_2 . On the other hand, the authors found a stable phase separation region in the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ type glass and could make an unique new type porous glass⁵⁻⁷⁾. This research was originally undertaken as part of the research project for effective utilization of "Shirasu", volcanic ash widely available in the southern part of Kyushu. The newly developed material was named "Shirasu" Porous Glass (SPG) to distinguish it from the conventional porous glass. This paper concerns the production process, properties and application techniques of SPG.

2. Principles of Porous Glass Production

It is known that the liquid-liquid immiscibility phenomenon occurs in some types of glass similar to that observed in a solution like water-phenol⁸⁾. This phenomenon is called phase separation (Fig. 1). It can be observed directly with naked eyes as opalization when glass is subjected to heat treatment at a temperature higher than the transition point and is rendered opaque.

If the size of the separation phase is extremely small, however, no apparent change can be recognized. Although phase separation is apparently a phenomenon similar to devitrification which crystallizes glass, it can not be easily distinguished from opalization, but can be clearly identified by electron microscopy and X-ray diffraction analysis. Phase separation of a glass, similar to that of the ordinary solution, may be thermodynamically accounted for from Fig. 2⁴⁾. While Gibbs energy of the mixture is smaller than that of the A or B component, it forms a stable, homogeneous mixture.

When the Gibbs energy of the mixture has a maximum, the system becomes unstable and

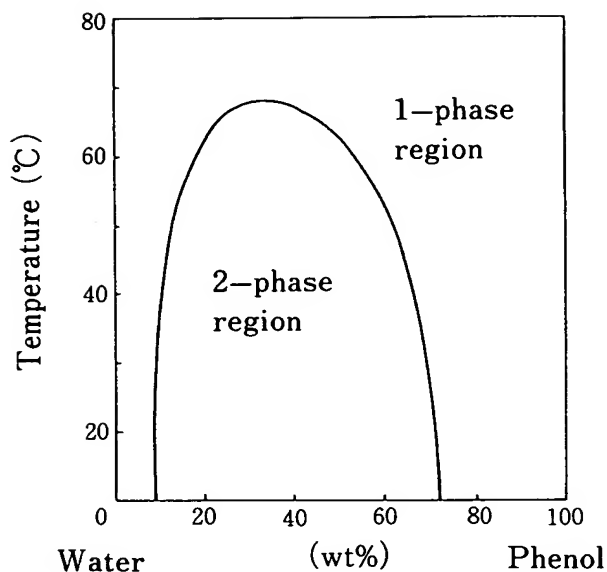


Fig. 1 Water-phenol intersolubility curve.

phase separation occurs between two stable phases represented by X_1 and X_2 compositions. The phase separation region in Fig. 3 was obtained by plotting the X_1 and X_2 of these separation phases measured at different temperatures. In a glass, the region enclosed with the immiscibility dome and the transition temperature is called to be a separation region. Since the viscosity of glass at the phase separation temperature is as high as more than 10^{12} times that of the ordinary solution system, the glass forms a unique separation phase structure that differs from that of the solution system. Phase separation of the former produces a discontinuous droplet phase or a continuous interconnected separation phase (Fig. 4). It is a matter of interest which type separation phase, droplet or interconnected, will be formed. Generally speaking, it depends on the volume fractions of the two phases, that is, the phase with a smaller volume forms the droplet phase and a phase with larger volume forms the matrix phase. The interconnected type phase forms when the volume fractions of two phases are close to

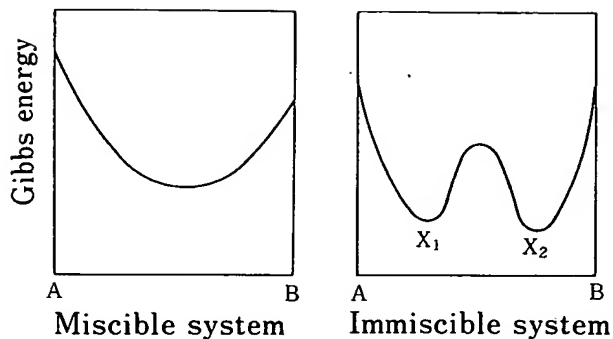


Fig. 2 Change in Gibbs energy in miscible and immiscible systems.

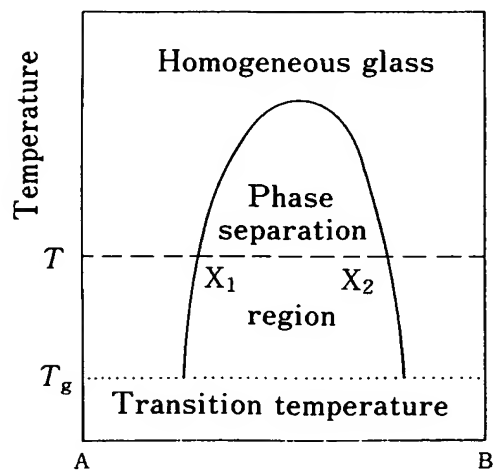


Fig. 3 Relation between glass phase separation region and temperature.

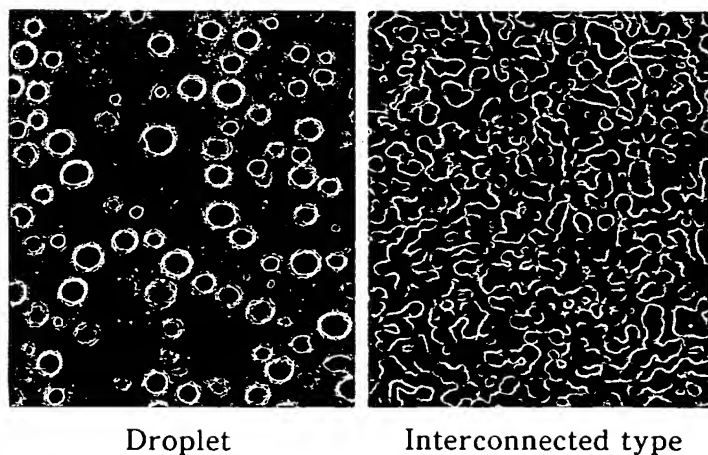


Fig. 4 Phase separation of droplet type and interconnected type.

each other. These separation phases generally grow to a coarser phase driven by the phase boundary energy in the neighborhood of the phase separation temperature as the temperature becomes higher and the processing time becomes longer.

Once the phase separation has occurred in the glass and if the separated phase is an interconnected type, it is possible to remove one phase by leaching, because there is a marked difference in solubility in a special solvent such as water, acid or others. Since the size of the separated phase can be controlled by the heat treatment temperature and duration, it is possible to make various kinds of porous glass with varied pore diameters.

3. Development of Porous Glass

Before discussing the development of SPG, a preview of the development of porous glasses which are now under way may be given as follows:

3.1 $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ type¹¹⁻¹³⁾

This is the oldest type of porous glass, widely known as porous Vycor glass. This type of glass was originally developed by the Corning Glass Works, USA, as a precursor of a high siliceous glass. It is playing an important role even today and many papers have been published on this material both in Japan and abroad. Disadvantage of this material is less water-resistant and less alkali-resistant because of the high content of silica in the glass skeleton.

3.2 $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ type

This type of glass is made as a phase-separative primary glass made from "Shirasu", lime and boric acid. This type of glass differs in chemical composition and property from the porous glass described in the preceding section. It can be applicable as separation membranes, adsorbing agents, packing materials for the high-performance liquid chromatograph (HPLC) and others. The preparation process will be described later.

3.3 $\text{Na}_2\text{O}-\text{CaO}-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ type

To eliminate the disadvantages of the porous glass made from $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ type glass, Eguchi et al¹⁴⁾ added components such as CaO , ZrO_2 and Al_2O_3 to their primary glass, and successfully developed a porous glass which excels in resistance to alkali. It is believed that ZrO_2 and Al_2O_3 contained in the glass skeleton inhibit erosion by alkali.

3.4 Crystallized glass type

The method of utilizing crystallized glass essentially differs from the normal porous glass made by utilizing the liquid-liquid immiscibility phenomenon, but its production process is similar to that of the normal porous glass. Materials made by this technique include the $\text{CeO}_2 \cdot 3\text{Nb}_2\text{O}_5$ ¹⁵⁾, mullite¹⁶⁾, $\text{SiO}_2-\text{TiO}_2$ ¹⁷⁾, $\text{SiO}_2-\text{AlPO}_4$ type porous crystallized glass¹⁸⁾.

3.5 Sol-gel type

The sol-gel method is a distinctive one, and is interesting in that it involves a possibility of producing glasses at low temperatures which have been difficult to make by the conventional dry melting method. Especially, ZrO_2 -rich porous glass¹⁹⁾ made with consideration to resistance to alkali eliminates the disadvantages of the conventional porous glass. However, it may be difficult to change the size of pores widely as compared with the phase separation method.

4. SPG Production Method

4.1 SPG production process

Fig. 5 shows the process for manufacturing SPG using the $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ type glass as a primary glass.

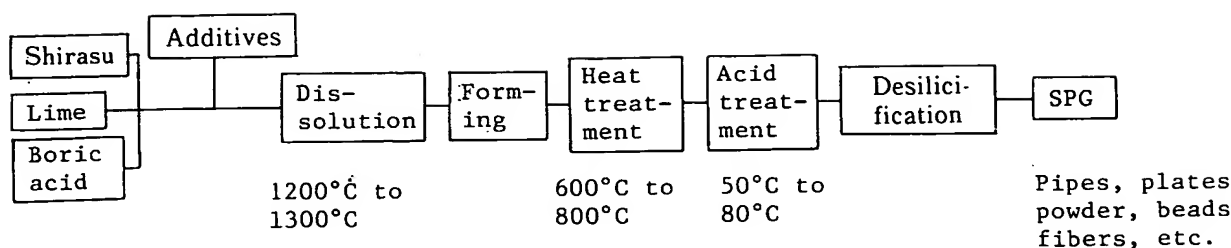


Fig. 5 SPG production process.

Table 1 Chemical composition of "Shirasu".

Component	wt%
SiO ₂	72.51
Al ₂ O ₃	13.65
Fe ₂ O ₃	2.14
CaO	1.26
MgO	0.29
Na ₂ O	3.04
K ₂ O	2.68
Ig. loss	4.54
Total	100.11

The basic process of separating the phase by heat treatment and dissolving the separation phase in acid is identical with that of Corning process, but the primary glass differs considerably in chemical composition because CaO and Al₂O₃ are added as major components. "Shirasu" used as raw material is volcanic ash glass and has the composition shown in Table 1.

"Shirasu" is the source of SiO₂ and Al₂O₃, but since it is a natural product, it cannot be avoided that it contains impurities such as Fe₂O₃ and others. Therefore, the primary glass has a light greenish color. When inclusion of impurities is not desired, "Shirasu" is substituted by silica sand and alumina. In many cases, however, "Shirasu" can be used as a raw material for the following reasons.

(1) Fe₂O₃ serves as an indicator of acid dissolution. (2) "Shirasu", substantially being a natural glass, enhances the vitrifying reaction rate. This makes it possible to prepare primary glass at relatively low temperatures of 1200°C to 1300°C and yet within a short time of 20 min to 60 min. (3) Since impurities can be dissolved in acid in a course of acid treatment, their existence can be ignored. (4) The raw material is very inexpensive and is almost inexhaustible.

After primary glass is formed into a tube, plate or fiber depending on the ultimate application of SPG, it is subjected to heat treatment at a temperature of 600°C to 750°C for several to scores of hours. This treatment causes the homogeneous primary glass to produce phase separation of SiO₂·Al₂O₃-rich glass and CaO·B₂O₃-rich glass. Since the CaO·B₂O₃ phase easily dissolves in acid, the desired porous SPG can be obtained by immersing the phase-separated glass into a dilute solution of hydrochloric acid.

4.2 Chemical composition

Table 2 shows the mixing ratio of raw materials. Table 3 shows the chemical composition of the primary glass and SPG prepared with this mixing ratio.

Table 3 also shows the composition of porous glass made by the Corning process for reference. Soda ash added to raw materials serves to adjust the rate of phase separation. In

Table 2 Mixing ratio of raw materials.

Raw material	(wt%)
Shirasu	50.79
Lime stone	22.53
Boric acid	22.28
Soda ash	4.40
Total	100.00

Table 3 Composition of primary glass and SPG

Component	Primary glass	SPG	Conventional material
SiO ₂	49.27	69.41	94.0 to 99.5
Al ₂ O ₃	9.47	12.81	0 to 0.5
B ₂ O ₃	15.70	6.90	0.2 to 6.0
CaO	17.12	2.12	
Na ₂ O	4.97	4.59	0.1 to less
K ₂ O	2.20	3.68	
MgO	0.19	0.03	
Fe ₂ O ₃	1.07	0.45	
Total	100.00	99.00	

addition, MgO is sometimes added to improve the working temperature of formation. Major components of SPG are SiO₂ and Al₂O₃, but it also contains B₂O₃ and alkali, and the distribution of chemical components by phase separation seems not so simple as may be supposed from the model given above. However, it differs greatly from porous glass made by the Corning process because it contains less SiO₂ more Al₂O₃ and other components.

4.3 Pore design

The size of the separated phase ultimately determines the pore size of SPG, and it is closely related to the heat treatment temperature and time. If this relation is clarified, it will become possible to design the pore size.

Fig. 6 is a micrograph taken by an electron microscope showing the relation between the temperature and the pore size when the heat treatment is made for 24 hours. The white bars in the micrographs represent 0.5 μ m. It can be seen here that the pore size increases markedly with increase in the heat treatment temperature. Fig. 7 shows the relation between the heat treatment time and the pore size when the primary glass is held at 700°C. It is clear that the pore size increases with the heat treatment time.

These facts reveal that the following relation exists between the pore size and the heat treatment conditions²⁰⁾.

(1) When the heat treatment time is held to be constant but the treatment temperature is changed

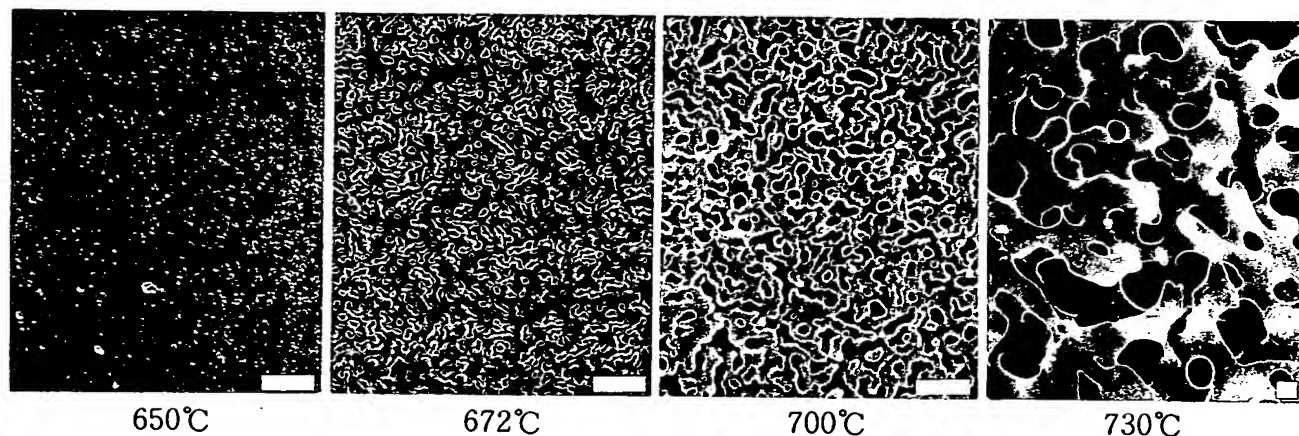


Fig. 6 Relation between heat treatment temperature and pore size.

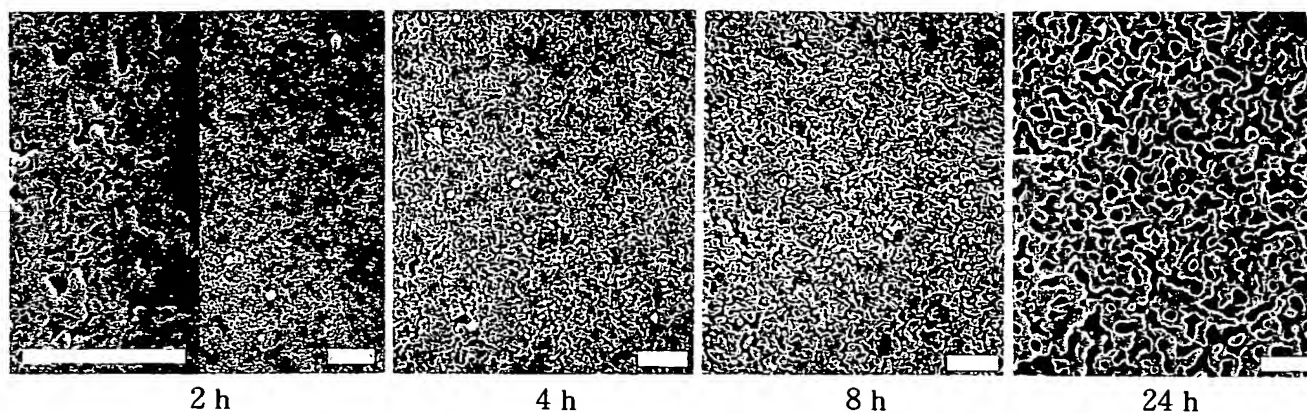


Fig. 7 Relation between heat treatment time and pore size.

$$\ln r = -E/2RT + C$$

(2) When the heat treatment temperature is maintained to be constant and the treatment time is varied

$$r = At^{1/2} - B$$

where r is the average pore radius, t the heat treatment time, T the heat treatment temperature, E the apparent activation energy, which is approximately $590 \text{ kJ} \cdot \text{mol}^{-1}$, R the gas constant, and A , B and C are the constants determined by the composition of primary glass.

4.4 Precipitation of colloidal silica

After minute examination of the porous glass made by the Corning method, Tanaka et al.²¹⁾ clarified that SiO_2 distributed in the separated phase precipitates in pores as a colloidal form during acid treatment. As pointed out by Haller as far back as in 1965²²⁾, this affects the speed of acid treatment and the performance of porous glass. Checking with SPG, the amorphous precipitates marked with arrows are observed at the inside of pores as shown in Fig. 8, and electron probe microanalysis (EPMA) reveals that the precipitate is composed of silica. The scale of Fig. 9 is $250 \text{ } \mu\text{m}$. Near the surface layer precipitates cannot be found, but

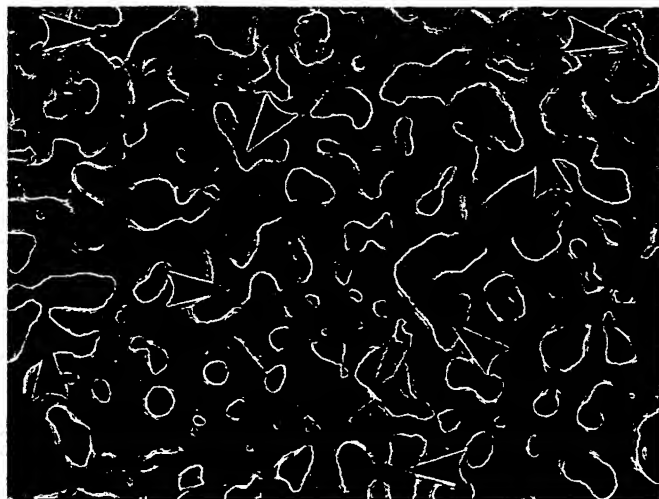


Fig. 8 Colloidal silica remaining in pores.

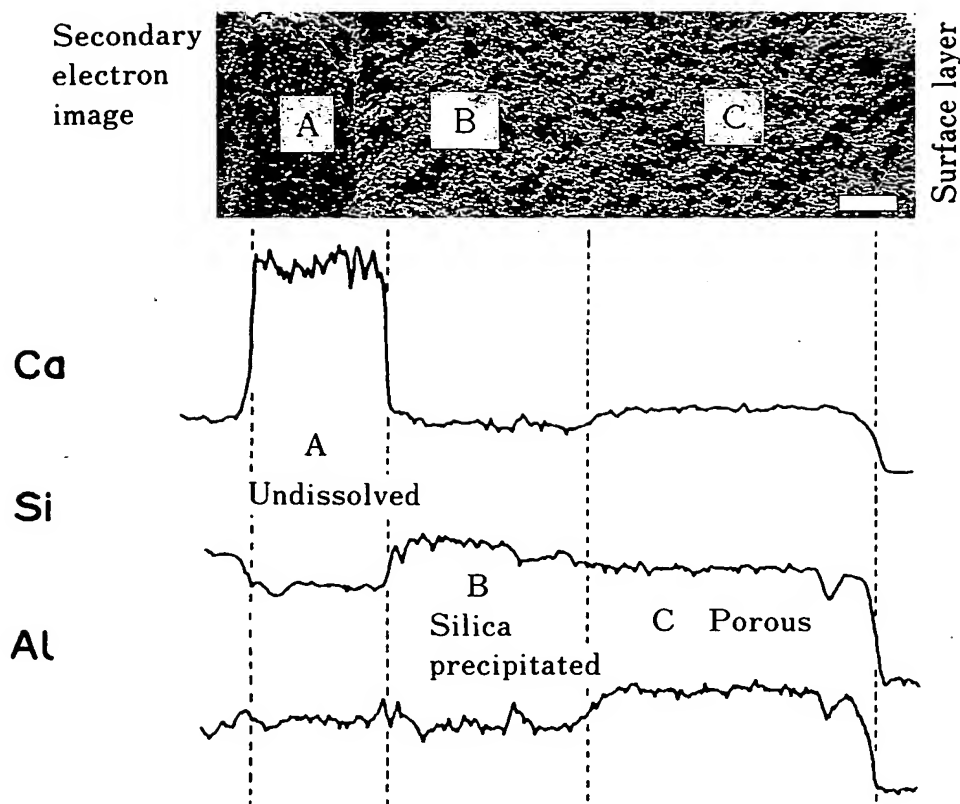


Fig. 9 X-ray microanalysis of phase separated glass in the course of acid leaching.

pores can be observed distinctly because its surface layer is in direct contact with acid into which colloidal silica can diffuse easily. In the interior of the phase-separated glass, dissolution of silica is so difficult that pores are filled with colloidal silica.

Since the presence of such precipitates often disturb smooth dissolution of its inner part of its separated phase, it is necessary to clarify the conditions under which silica precipitates.

Fig. 10 shows the relation between BET surface area of SPG and acid concentration used for leaching maintaining the ratio of glass to acid solution to be constant. The fact that the higher the acid concentration the larger surface area suggests that the more colloidal silica exists the more interior of the separated phase. To the silica precipitating conditions are also related the temperature of acid and the bath ratio. From these facts it can be concluded that the precipitating conditions are determined by the solubility of silica in the treatment solution and that it should be possible to prevent the precipitation of colloidal silica by providing an environment which causes silica to dissolve. In many cases, small amount of colloidal silica cannot be removed by its an treatment. The colloidal silica remained in pores, however, can be removed by immersing the acid leached glass into 0.2 to 0.5 mol·dm⁻³ sodium hydroxide solution because of SPG contains much Al₂O₃ and excels in resistance to alkali.

5. Properties of SPG

5.1 Physical properties

One of the features of SPG is the unique porous microstructure, which is closely related to mechanical properties such as strength and others.

Fig. 11 (a) is a micrograph (scale 10 μm) taken by an electron microscope, and Fig. 11

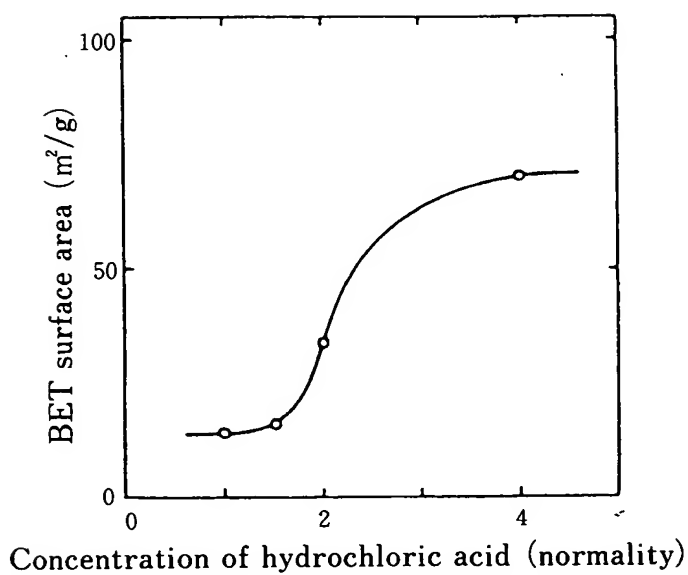
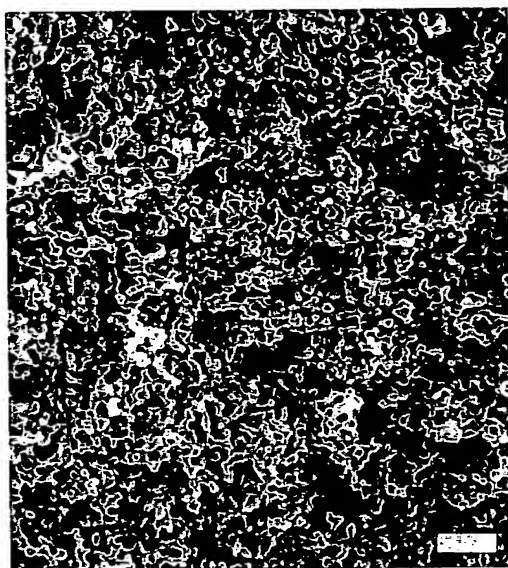
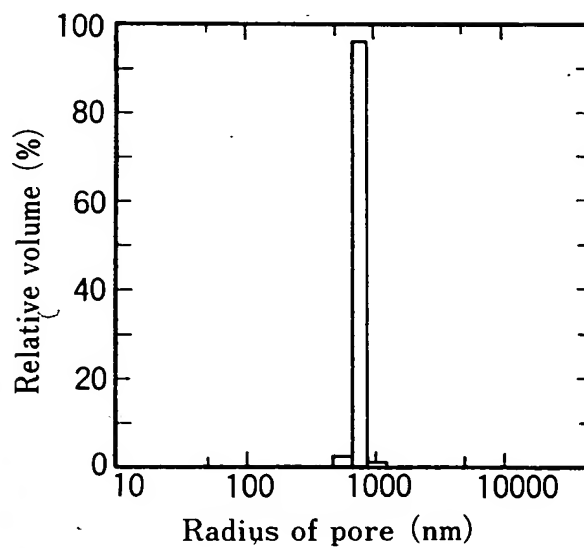


Fig. 10 Acid concentration and BET surface area of SPG.



(a) Micrograph taken by electron microscope.



(b) Pore size distribution.

Average pore radius : 725 nm, pore volume : $0.57 \text{ cm}^3 \cdot \text{g}^{-1}$, porosity : 59%.

Fig. 11 Pore structure of SPG.

(b) shows the pore distribution measured by a mercury penetration porosimeter. As can be seen in Fig. 11 (a), SPG is made up of many perforated pore structure interconnected with each other in a complex manner.

The pore size of SPG can be sharply designed within a wide range of several nanometers to 10 micrometers. Thus, one of the largest features of SPG is that the pore diameter can be controlled exactly over a wide range from submicron to micron order.

Table 4 shows the physical properties of the typical SPG tube. The mechanical strength is generally higher than that of other ceramic porous materials having the same porosity.

The reason why the SPG has much a higher mechanical strength is caused by the fact that stress does not concentrate at any point because pore size of SPG distributes in narrow range as a result of precise pore control and that the skeleton of SPG is made up of continuous glass networks, compared with the skeleton of ceramics which is primarily joined by grain boundaries having many structural defects²³⁾.

Table 4 Physical properties of SPG.

Pore diameter	200 to 10000 nm
Porosity	50 to 60%
Pore volume	0.4 to 0.6 cm ³ ·g ⁻¹
Specific surface area	0.2 to 8.0 m ² ·g ⁻¹
True density	2.5 g·cm ⁻³
Thermal expansion coefficient	60×10 ⁻⁷ K ⁻¹
Heat resisting temperature	650°C
Compressive strength	2000 to 3000 kgf·cm ⁻²
Bending strength	710 to 840 kgf·cm ⁻²

5.2 Chemical properties

It has often been pointed out that the conventional high silica porous glass has less resistance to water and alkali²⁴⁾. To overcome these problems attempts have been made by adding a small amount of TiO₂ and ZrO₂ to primary glass or by treating porous glass with AlCl₃²⁵⁾. Since SPG contains a large amount of Al₂O₃ of more than 10%, we can surmise that the skeleton of SPG excels in resistance to water and alkali.

Fig. 12 shows the water-resistance of SPG in terms of the amount of dissolution of SiO₂ and Na₂O in water. For SiO₂, small detectable amount is found, and for Na₂O amount of dissolution is negligibly small. These facts show that of SPG has a high water-resistance compared with the conventional porous glass. Fig. 13 shows the variation in the mechanical strength of SPG which has been subjected to the hydrothermal treatment at 100°C to 200°C.

Although some decrease in the compressive strength is found for the material treated at 200°C, and only small extent of change in Young's modulus is observed. These facts show that the effects of hydrothermal treatment are small.

Regarding chemical resistance, SPG is hardly eroded by any chemicals except hydrofluoric acid, and it shows particularly resistance to strong acids and organic solvents. The surface of SPG is hydrophylic because there are functional groups such as -SiOH, -BOH, etc. Properties of the surface can be changed by chemical modification by the use of these functional groups. This property is of great advantage to the production of packing materials for

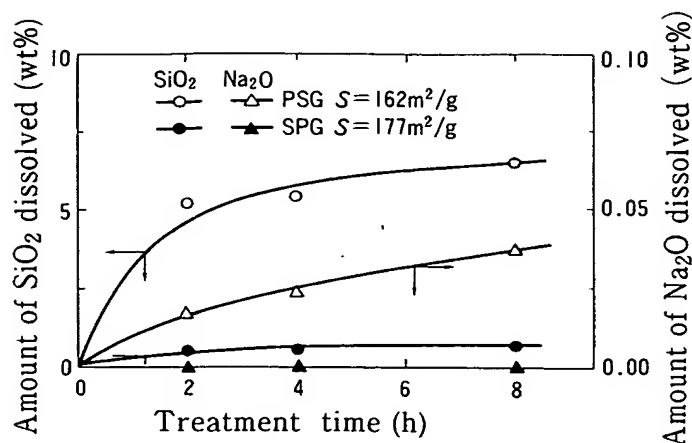


Fig. 12 Water-resistance of SPG at 95°C.

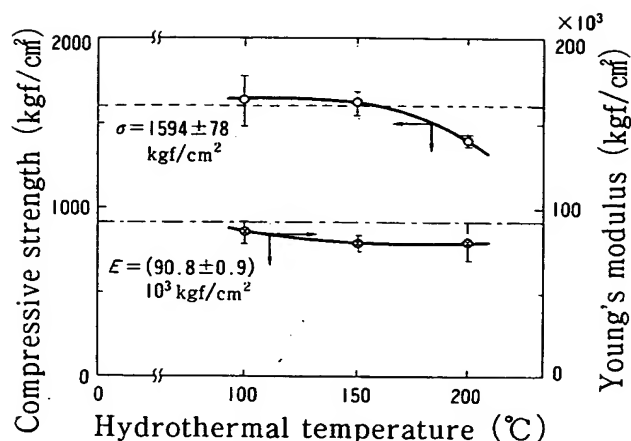


Fig. 13 Influence of hydrothermal treatment upon mechanical strength.

the chromatography, immobilized enzyme, immobilized bacterizer²⁶⁾, and nucleic acids²⁷⁾ by the Merrifield method.

6. Conclusion

Porous glasses include sintered porous glass, foam glass, micro hollow spheres, and others as well as above mentioned porous glass made by the phase separation. But the limited space does not allow to describe each of these materials here. One of the remarkable characters of SPG compared with those of other porous glass is that concentrated pores can be designed precisely over a wide range of its diameter. Future commercialization of porous glasses including SPG depends on how far new applications can be extended by taking advantage of the features of these materials.

References

- 1) S. Yamanaka et al, *Functional Materials*, 4[5], 1 (1984).
- 2) A. Makishima, *Surface*, 21 [2], 105 (1983).
- 3) S. Sakka, *Chemical Equipment*, No.3, 52 (1983).
- 4) T. Sakaino, "Porous Materials" edited by R. Kondoh, Gihodo Publishing Co., p. 268 (1973).
- 5) T. Nakashima et al, US Pat. 4657875 (1987).
- 6) T. Nakashima, Y. Kuroki, *Publication of Patent Application*, 25618-1987.
- 7) T. Nakashima, M. Shimizu, *Ceramics Japan*, 21, 408 (1986).
- 8) R. Hujishiro, A. Kuroiwa, "Property of Solution I" (Modern Physical Chemistry Course 7), Tokyo Kagaku Dojin, p.125 (1966).
- 9) I. Yasui, H. Kawazoe, "High Function Glass" (Material Technology 14), Univ. of Tokyo Publishing Society, p.140 (1985).
- 10) T. Sakaino, "Porous Materials" edited by R. Kondoh, Gihodo Publishing Co., p.269 (1973).
- 11) H. D. Hood and M. E. Nordberg, US Pat. 2215039 (1940).
- 12) J. J. Hammel et al, US Pat. 3843341 (1974).
- 13) K. Eguchi, Abstracts of 5th Ionics Polymer Lecture, p.1 (1981).
- 14) K. Eguchi et al, Abstracts of Lecture at Annual Meeting of Ceramics Society, p.493 (1987).
- 15) M. A. Res et al, *J. Am. Ceram. Sci.*, 65, 184 (1982).

- 16) G. H. Beat et al, US Pat. 3881944 (1975).
- 17) T. Kokubu, M. Yamane, *J. Material Science*, 20, 4309 (1985).
- 18) S. Morimoto et al, Abstracts of Lectures at 1987 Annual Meeting of Ceramics Society, p.497 (1987).
- 19) M. Nogami, *Yogyo-Kyokai-Shi*, 93, 195 (1985).
- 20) T. Nakashima, Y. Kuroki, *Nippon Kagaku Kaishi*, 1981, 1231.
- 21) H. Tanaka et al, *Yogyo-Kyokai-Shi*, 91, 384 (1983).
- 22) W. Haller, *J. Chem. Phys.*, 42 [2], 686 (1965).
- 23) T. Nakashima, M. Shimizu et al, Abstracts of Lectures at 24th Ceramic Basic Discussion, p.130 (1986).
- 24) S. Sakka, *Chemical Industry*, 33 [2], 159 (1982).
- 25) E. V. Ballou et al, *Nature Phys. Sci.*, 229, 123 (1971).
- 26) H. Korai et al, *Publication of Patent Application*, 169904-1985.
- 27) K. Imada et al, to be published.